Buzzi

INDUSTRIAL CHEMICAL DIVISION

Stauffer CHEMICALS

Stauffer Chemical Company

P.O. Box 428, Lewiston Rd. / Niagara Falls, N.Y. 14302 / 716 BU 5-8261-62-82

OK

March 5, 1974

Mr. Ernest Gedeon
Assistant Commissioner of Environmental Health
Niagara County Health Department
525 Bewley Building
Lockport, New York 14094

Dear Mr. Gedeon:

Attached are three copies of the emission test report on our source C-15, Metal Chlorides Main Scrubber. The test data show the emissions to be less than the allowable.

Very truly yours,

Samuel Weiss

/s/ Kenneth Hoffman
Kenneth Hoffman,
Technical Superintendent

KH:mf

cc: E.L. Conant
S.H. Friedman
D.G. Frye
J.W. Call
T.E. Purcell

SMC-789 0710

STAUFFER CHEMICAL COMPANY

March 5, 1974

Emission Test on Source C-15
Metal Chlorides Main Scrubber Stack

The test as reported herein was made to demonstrate compliance with the emission limits as specified in the Certificate of Environmental Rating (AIR 112) dated July 13, 1972. The dates of testing were Feb. 22 and 23, 1974. The test consisted of three individual one-hour periods. Personnel involved in the test were:

Kenneth Hoffman, Stauffer - Technical Superintendent
Maurice Holmes, Stauffer - In direct charge of test
James Sayes, Stauffer
Edward Phelan, Stauffer
Ross Salimbene, Niagara County Health Dept.

Process Description

Silicon and zirconium tetrachlorides are made by chlorination of silicon and zirconium ores. Carbon monoxide is a product of the reaction, and passes through refrigerated condensers to remove as much of the volatile silicon tetrachloride as possible. This carbon monoxide along with small amounts of silicon tetrachloride, nitrogen, carbon dioxide, unreacted chlorine, and phosgene (formed by the reaction of chlorine with carbon monoxide) passes through a scrubbing system and then is flared. The scrubbing system consists of a packed scrubber using once-through sodium hydroxide under pH control, followed by a venturi-type scrubber using a recirculating system with a small fixed sodium hydroxide makeup. The clean gases (carbon monoxide, nitrogen, and some of the carbon dioxide) then pass through a seal pot (water or very dilute sodium hydroxide solution) and up the flare stack. Two blowers in series provide the motive power for the high energy venturi scrubber and system resistance to flow. A chlorine analyzer on the clean gas detects system malfunctions and sounds an alarm. The process is continuous.

Attached is a Process Flow Diagram, Dwg No. 72-11D (Rev. 10-11-73). The exact nature and quantities of reactants and products are proprietary information, and are not included herein.

Equipment Specifications

Main Scrubber - Manufactured by the Pfaudler Co., of Stauffer design, 3 ft. dia. x 14 ft. high, packed, rated 1000 cfm with 5"H20 pressure drop.

Venturi scrubber - Manufactured by American Air Filter Co., Size 2 Kinpactor and size 19 cyclonic separator. Manual adjustable throat damper. Rated to handle 500-2000 cfm, at vacuums up to 75" W.G.

Blowers (2) - Manufactured by Garden City Fan Co., No. PBF-326-8-25, 25 HP motor, mechanical seal on shaft, 3500 rpm. To handle approx. 1800 cfm at a differential pressure of about 38" W.G. (each, at normal operating conditions).

Flare stack - Manufactured by John Zink Co., Model STF-J-6, rated 900 cfm with pressure drop of 7" W.G. Total height to tip (above grade) - 100 ft.

The partially cleaned gas from the main (first) scrubber enters the venturi scrubber, along with approximately three times its volume of gas recycled back from the blower discharge. A dilute NaOH solution is pumped into the throat of the venturi, where intimate contact occurs between the gas and liquid. This mixture then enters the cyclonic separator, the liquid flowing back to the pump supply tank, and the gas going to the two blowers in series. From the blowers part of the gas recycles and part exits to the stack. The recycle gas is controlled automatically to maintain a fixed differential pressure across the venturi scrubber (generally in the range of 45 inches water) to insure a uniform high scrubbing efficiency. The gas to the stack passes first through a seal pot (containing water or dilute NaOH), then

Equipment Specifications (continued)

through a flame arrestor, a molecular seal, and then the burner proper. Ignition is assured by three pilots fueled with natural gas, and equipped with flame-out warning. A gas sampling and analysis system is provided to warn of high chlorine or oxygen in the gas in the system.

Process Data and Operating Conditions

Detailed data on plant processing conditions cannot be submitted because of its confidential nature. However, general information and operating data for the pollution control system are as follows:

The chlorination of the silicon and zirconium ores was proceeding in a normal manner, at approximately full capacity. The reaction was fairly efficient, so that phosgene and excess chlorine entering the scrubbing system were nominal in quantity. Conditions for the venturi system and stack were as follows:

	Test 1	Test 2	Test 3
Venturi Δ P, in.W.G.	44	42	51.5
Caustic flow to pump supply tank, gpm	2	2	2
Water flow to pump supply tank, gpm	1	1	1
Gas flow to stack (dry), SCFM	311	406	362

Variations in the quality of the ores are not known to affect the stack emissions. Actually, variations in the chemical composition of the ores are very small and have no noticeable affect on plant operations.

Stack Testing and Analytical Procedures

Equipment and methods used are described in our application for approval of test methods, dated Oct. 10, 1973 ("Re: E-691636 Testing of Source C-15, Metal Chlorides Main Scrubber Stack"), except for the following modifications:

1. A preliminary trap was used ahead of the impinger train to segregate any condensate coming out of the sample line. The contents were evaluated separately and included in the totals.

2. Four Greensburg-Smith impingers were used instead of three, each filled with 100 ml of 1 N NaOH solution. All 4 impingers and the desicant dryer were immersed in an ice bath. The entrainment separator shown between the last impinger and the dryer was not in the ice bath, and remained perfectly clean (no catch).

3. The vacuum pump was checked independently for leakage prior to testing by subjecting the entire pump (in a sealed system including a 5 gal. bottle) to a vacuum of 15" mercury. The pump was running with its bypass open. In 20 min., the vacuum had dropped 0.3" Hg, a leakage rate of about .0003 SCFM.

4. The system was checked for leak tightness by disconnecting the Teflon tubing at the process sampling point, inserting a plug in the tubing, and pulling a vacuum of 15" Hg with the pump. In 10 min. the dry test meter showed no change in reading. Estimating a net readability of 0.02 cu.ft., the leakage rate was not higher than 0.002 CFM. This test was performed prior to each of the three tests.

5. The sample line was conditioned for 30 min. prior to each test by venting through the line to atmosphere, a pressure of about 15" water being present in the process.

Stack Testing and Analytical Procedures (continued)

6. The gas temperature was read both into and out of the dry test meter and averaged for the calculations.

7. The dry test meter was checked for accuracy by collecting the throughput in an inverted water-filled 5-gal. bottle. In the calculations, appropriate corrections were made for pressure drops in the system, moisture pickup by the gas as it entered the bottle, etc. Checks were made at an orifice ΔH of 0.5" and 4.0" (compared to the test ΔH of 1.2"), and the meter was accurate to within $\pm$ 0.04% at both rates.

Test Results

	Test 1	Test 2	Test 3	Ave.	Allowable
Emission Rates, lb/hr.					
Chlorine	8.3	nil	nil	2.8	22
Silicon Tetrachloride	.01	.01	.00	.01	5.8
Phosgene	8.4	2.4	0.8	3.9	8.0

The flare burned with a pale pinkish flame, discernible as such with an overcast sky but practically invisible on a sunny day. The luminosity was judged to be insufficient for temperature measurement with an optical pyrometer.

Kenneth Hoffman

Kenneth Hoffman,
Technical Superintendent

Attached:

Data Sheets	2 sheets
Sample Calculations	3 sheets
Emission Control Flow Sheet	Dwg. 72-11D Rev. 10-11-73

LOCATION [illegible]
OPERATOR
DATE [illegible]
RUN NO. 1 & 2

METER ΔH
C FACTOR
AMB. TEMP. #1 [illegible] #2 [illegible]
BAR. PRESS. #1 28.56" #2 28.5[illegible] 725.4mm 725mm

HEATER SETTING none
PROBE LENGTH, IN. none
NOZZLE DIA., IN. .25"
PROBE HEAT. SETTING none

STACK CROSS SE[illegible]

TRAVERSE POINT	TIME	SAMPLING TIME MIN. θ	STATIC PRESSURE P_S IN. Hg	STACK TEMP T_S °C	STACK ~~VEL. HEAD~~ ORIFICE ΔP_S " OIL*	ORIFICE METER ΔH IN. H_2O	GAS VOLUME V_m FT^3	GAS TEMPERATURE METER IN T_m IN °C	METER OUT T_m OUT °C	LAST IMP. °C	SAMPLE BOX TEMP. °F	[illegible] H_2O	N[illegible]
NONE	11:05AM	([illegible]	[illegible])			—	—						
"	11:53		2.0**	51.0	20.5	1.2	182.39	18.0	16.0	9.0	ICE BATH	1.7	[illegible]
"	12:04PM		2.0	51.5	19.25	1.18	—	21.0	16.0	8.5	"	1.6	
"	12:14		1.9	52.0	17.25	1.19	—	24.0	18.0	9.0	"	1.6	
"	12:24		2.0	55.0	19.00	1.2		25.0	18.5	9.0	"	1.65	
"	12:34		2.0	57.0	19.00	1.19		26.0	19.0	9.0	"	1.65	
"	12:44		2.1	58.0	19.50	1.19		27.0	19.0	9.0	"	1.65	
"	12:52	[illegible]			[illegible] 19.1		186.03	27.0	19.0	9.5	"	1.65	
							33.64	21.6°C avg					
NONE	2:50PM	([illegible]	Line purge 30 min)										
"	3:23 "		2 5/8"	51.0	30.0	1.20	186.46	15.0	16.0	11.0	"	1.6	[illegible]
"	3:33 "		2 5/8	51.0	29 1/4	1.21	—	17.8	16.0	8.0	"	1.65	
"	3:43 "		2 5/8	49.5	28.0	1.20	—	19.8	16.0	8.0	"	1.65	
"	3:53		2 5/8	47.0	29.0	1.20	—	20.4	16.2	8.0	"	1.65	
"	4:03		2 5/8	48.5	29 1/4	1.21	—	20.4	16.2	8.5	"	1.65	
"	4:13		2 5/8	50.0	31 1/4	1.22	—	20.4	16.2	7.6	"	1.65	
"	4:23	60 min	2 5/8	5[illegible]	30.5	1.20	220.63	20.4	16.2	7.5	"	1.65	
							34.17	18° avg.					
	* .826 MANOMETER OIL			** + 1 1/4" H_2O ON SUCTION SIDE									
TOTAL								AVG.	AVG.				

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PLANT [illegible] METER NO. [illegible]

LOCATION N.A. FALLS METER ΔH ______ HEATER SETTING [illegible]

OPERATOR ______ C FACTOR ______ PROBE LENGTH, IN. ______

DATE 2/25/74 AMB. TEMP. -4°C NOZZLE DIA., IN. .25"

RUN NO. 3 BAR. PRESS. 29.45 PROBE HEAT. SETTING none

STACK CROSS SE[CTION]

TRAVERSE POINT	TIME	SAMPLING TIME MIN. θ	STATIC PRESSURE P_S IN. Hg	STACK TEMP T_S °C	STACK ~~VEL. HEAD~~ ORIFICE ΔP_S" OIL*	ORIFICE METER ΔH IN. H_2O	GAS VOLUME V_m FT^3	GAS TEMPERATURE METER IN T_m IN °C	METER OUT T_m OUT °C	LAST IMP. °C	SAMPLE BOX TEMP. °F	METER PRESS "H_2O	NOTES
	1:20 PM	Started line purge 10 min + 10 min											
	3:06 "		[illegible]	51.0	23.5	1.20	220.81	15°	15	9.0	ICE BATH	1.65	started sample
	3:16 "		2 3/8 **	50.5	23.5	1.19	—	16	15.0	8.0	"	1.65	
	3:26		2 3/8	52.0	23.5	1.20	—	20.0	15.0	9.5	"	1.65	
	3:36		2 3/8	50.0	23.0	1.20	—	22.5	16.0	10.2	"	1.65	
	3:46		2 3/8	50.5	23.0	1.19	—	23.8	17.0	11.0	"	1.65	
	3:56		2 3/8	50.2	22.75	1.20	—	24.0	18.0	10.5	"	1.65	
	4:06	60 min	2 3/8	50.2	23.0	1.20	253.56	24.2	18.2	10.5	"	1.65	end sample
							32.75	19.1 avg.					
	* MANOMETER OIL SP.GR. 0.826				** +1 3/4" H_2O ON SUCTION SIDE								
TOTAL								AVG.	AVG.				

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SAMPLE CALCULATIONS

Reference: Perry's Chemical Engineers Handbook, 4th Ed.

Orifice - 2.500" dia. in 4" Sched. 80 std. iron pipe

Fig. 5-16: $B = \frac{D_2}{D_1} = \frac{2.500}{3.826} = .653$

K (at vena contracta) = .675

Upstream pressure measurement - mercury manometer with 1-1/4" water on top of mercury on suction side

Corrected press. $= 2.0 + \frac{1.25}{13.58} + 28.56 = 30.65$ "Hg abs.

Orifice ΔP - S.G. of manometer oil corrected for ambient temp. = .836

$$\Delta P = \frac{19.1 \times .836}{13.58} = 1.176 \text{ "Hg}$$

Fig. 5-13: $r = \frac{p_2}{p_1} = \frac{30.65 - 1.176}{30.65} = .962$

$k = \frac{Cp}{Cv}$ (for CO) = 1.4 (Table 3-180)

$\frac{1-r}{k} = \frac{1 - .962}{1.4} = .0268$ $B^2 = .653^2 = .426$

$Y = .985$

$$A_2 = \frac{\pi \; 2.5^2}{4 \times 144} = .0341 \text{ ft}^2$$

Let P = abs. press. water at upstream cond., "Hg (Table 15-3)
V = spec. vol. water at upstream cond., cf/lb. (Table 15-3)
P = 4.5 , V = 157

Fract. water by vol. $= \frac{4.5}{30.65} = .1468$

Density CO = .0781 lb/cf at 0°C, 1 atm (Table 3-48)

Ave. gas temp. = 54.1°C

Gas density at orifice $= \left[.0781 \times \frac{273.1}{273.1 + 54.1}(1 - .1468) + \frac{1}{157}\right] \frac{30.65}{29.92}$
$= .0635$ lb/cf

Eqn. (5-9): $w = KYA_2 \sqrt{2 g_c (p_1 - p_2) \rho_1}$

$$= .675 \times .985 \times .0341 \sqrt{32.16 \times 2 \times 1.176 \times \frac{14.7}{29.92} \times 144 \times .0635}$$

$$= .418 \text{ lb/sec.}$$

CFM orifice cond.= $.418 \times 60/.0635 = 395$

$$\text{SCFM } (70^{\circ}\text{F, 1 atm}) = 395 \times \frac{30.65}{29.92} \times \frac{(460 + 70)}{1.8\,(273.1 + 54.1)} = 364$$

$$\text{SCFM dry gas} = 364\,(1 - .1468) = 311$$

Sample Gas Volume

Metered vol. 33.64 cu. ft.

Ave. temp. at meter = 72°F

$$\text{Meter press. (dischg.)} = \text{Barometer} + \frac{\Delta H \ (\text{"}H_20)}{13.58}$$

$$= 28.56 + \frac{1.19}{13.58} = 28.65 \text{ "Hg}$$

$$\text{Dry gas thru meter} = 33.64 \times \frac{460 + 70}{460 + 72} \times \frac{28.65}{29.92} = 32.09 \text{ SCF}$$

$$\text{Factor to stack} = \frac{311 \times 60}{32.09} = 581 \text{ lb/hr. contaminant per lb. in sample}$$

Analytical Data

Typical avail. Cl2 analysis (Trap No. 1):

Contents of trap washed into volumetric flask and built to 250 ml. 5 ml. aliquot taken for analysis.
Titration 22.75 ml .025 N sodium thiosulfate

$$\text{Avail. Cl2 content} = 22.75 \times .025 \times \frac{35.46}{1000} \times \frac{250}{5} = 1.008 \text{ g.}$$

Typical total Cl^- analysis (Trap No. 1):

10 ml aliquot out of 250 ml taken.
Titration 10.00 ml .1449 ml $AgN0_3$,
2.06 ml .1552 ml KSCN

$$\text{Total } Cl^- = (10.00 \times .1449 - 2.06 \times .1552) \times \frac{35.46}{1000} \times \frac{250}{10} = 1.001 \text{ g.}$$

Typical Si02 analysis (Trap No. 1):

10 ml. aliquot was taken from the 250 ml, reagents added and diluted to 100 ml, then a 5 cm cell was filled with this solution. An absorbance of .075 was obtained. A blank was run, consisting of the same reagents in a similar impinger; this resulted in an absorbance of .065. Referring to the calibration curve, obtained with a 1 cm cell, using an absorbance of $\frac{.075 - .065}{5/1}$ or .002, a concentration of .053 μg/ml is obtained. Total Si02 in trap = $.053 \times 10^{-6} \times \frac{100}{10} \times 250 = .0001$ g.

Summary of analysis:

	Avail. Cl_2	Total Cl^-	SiO_2
Trap No. 1	1.008	1.001	.0001
Impinger No. 1	1.970	4.179	.0002
Impinger No. 2	2.336	4.467	.0009
Impinger No. 3	1.162	1.413	.0003
Impinger No. 4	.014	.140	.0003
Trap No. 2	none	none	none
Total	6.490 g.	11.200 g.	.0018 g.

$$SiCl_4 \text{ equiv. to } SiO_2 = .0018 \times \frac{170}{60} = .0051 \text{ g.}$$

$$Cl^- \text{ from } SiCl_4 = .0051 \times \frac{142}{170} = .00426 \text{ g.}$$

$$Cl^- \text{ from } COCl_2 = 11.200 - 6.490 - .00426 = 4.706 \text{ g.}$$

$$COCl_2 = 4.706 \times \frac{99}{71} = 6.562 \text{ g.}$$

Emissions:

$$\text{Chlorine} = 6.490 \times \frac{1}{453.6} \times 581 = 8.31 \text{ lb/hr.}$$

$$COCl_2 = 6.562 \times \frac{1}{453.6} \times 581 = 8.41$$

$$SiCl_4 = .0051 \times \frac{1}{453.6} \times 581 = .01$$

Summary of Analyses
2nd Hour of Test:

	Avail. Cl_2	Total Cl^-	SiO_2
Trap No. 1	none	.058	.00003
Impinger No. 1	"	.478	.00001
Impinger No. 2	"	.268	.00058
Impinger No. 3	"	.161	.00053
Impinger No. 4	"	.103	.00042
Trap No. 2	"	none	none
Total	none	1.068 g.	.00157 g.

3rd Hour of Test:

Trap No. 1	none	.034	.00004
Impinger No. 1	"	.157	.00015
Impinger No. 2	"	.105	.00019
Impinger No. 3	"	.069	.00015
Impinger No. 4	"	.045	.00019
Trap No. 2	"	none	none
Total	none	.410 g.	.00072 g.

* PROTECT AGAINST FREEZING

TIE-INS REQ'D

1 — 4" POND WATER RETURN
2 — 2" WATER TO CAUSTIC LINE
3 — 1" CAUSTIC RECOVERY
4 — 8" SCRUBBER OUTLET
5 — 4" SCRUBBER SEAL LEG
6 6A — 2" WATER TO ENTOLETER / SEAL POT
7 7A — 1" NaOH TO ENTOLETER / SEAL POT
8 — 1½" NITROGEN
9 — 1" STEAM (HI PRESSURE)
10 — 1" AIR
11 — 1½" NATURAL GAS

MCS - MANUAL CONTROL STATION
PSI - PRESSURE SWITCH, INDICATING

ISSUED FOR CONSTRUCTION
ISSUE NO.
DATE

ISSUED FOR APPROVAL
ISSUE NO.
DATE

STAUFFER CHEMICAL CO., INC.
ENGINEERING DEPARTMENT. DOBBS FERRY, N. Y.

CO FLARE SYSTEM
METAL CHLORIDES PLANT
NIAGARA FALLS, N.Y.

D'WN. BY N.S.	CH'K'D. BY	APP'D. BY	SCALE
DATE 12-23-71	DATE	DATE 1/4/72	
D'WG. NO.	WORK ORDER	ISSUE	FILE NO.
80	NF TASK	A 2-7-72	72-11D

REV. 8-30-73 KH 10-11-73

SMC-789 0719